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(71) Applicant: SUMITOMO CHEMICAL COMPANY, LIMITED  
15 Kitahama 5-chome Higashi-ku  
Osaka-shi Osaka-fu(JP)

(72) Inventor: Hanji, Katsumi  
8-1-208 Natsumidai-1-chome  
Funabashi-shi(JP)

(72) Inventor: Kawai, Kiyoshi  
6-1-738, Kitajocho-4-chome  
Toyonaka-shi(JP)

(74) Representative: Vossius Vossius Tauchner Heunemann  
Rauh  
Siebertstrasse 4 P.O. Box 86 07 67  
D-8000 München 86(DE)

(54) Solid catalyst component for olefin polymerization.

(57) A solid catalyst component for olefin polymerization comprising a hydrocarbon-insoluble product (III) obtained by reacting

(A) a silicon compound selected from the group consisting of

(1) silicon compounds represented by the general formula  $R^1R^2R^3Si$ ; wherein  $R^1$ ,  $R^2$  and  $R^3$  are each an alkyl, cycloalkyl, aralkyl, aryl; alkoxy, aryloxy, or hydroxyl group or a halogen or hydrogen atom; and  $a$ ,  $b$  and  $c$  are numbers defined by the formulas  $0 \leq a, b, c, \leq 4$  and  $a + b + c = 4$ ; and

(2) silicon compound containing the linkage Si-O-Si and polymers thereof with

(B) a compound of a transition metal of Groups IVa, Va and VIa of the periodic table to form a reaction mixture (I), further reacting the reaction mixture (I) with

(C) an organomagnesium compound selected from simple organomagnesium compounds and hydrocarbon-soluble complexes thereof with an organometallic compound capable of solubilizing said organomagnesium compounds

to produce an intermediate product (II), and contacting the intermediate product (II) with

(D) a halogen-containing compound of a transition metal of Groups IVa, Va and VIa of the periodic table, to form the hydrocarbon-insoluble product (III).

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SUMITOMO CHEMICAL COMPANY, LIMITED  
OSAKA, JAPAN

SOLID CATALYST COMPONENT FOR OLEFIN POLYMERIZATION

1           This invention relates to a novel high-activity  
solid catalyst component for Ziegler catalyst system  
for use in olefin polymerization and, from a different  
viewpoint, to a process for the preparation of said  
5 solid catalyst component.

When an olefin is polymerized by using the  
solid catalyst component of this invention as the  
transition metal catalyst component of the Ziegler  
catalyst system, the polymer yields per unit quantity  
10 of the transition metal as well as per unit quantity  
of the solid catalyst component is so much increased  
that it becomes unnecessary to remove the catalyst  
residue from the polymerizate after completion of the  
polymerization. Moreover, the polymer build-up on  
15 the wall of polymerization vessel during polymerization  
is very little and there is formed in slurry or gas-  
phase polymerization a powdered polymer in the form of  
approximated sphere or elongated sphere (ellipsoid),  
which has a narrow particle size distribution, a high  
20 bulk density, and a desirable flowability. Further,  
according to this invention, it is possible to control  
the molecular weight of a polymer within the range from  
narrow to broad by suitably selecting the material ratio  
of components used in preparing the catalyst and  
25 the type of compounds of transition metals of Groups

1 IVA, Va and VIa of the periodic table .

It is needless to say that in the production of olefin polymers, a highly active catalyst has a high utility value from the industrial viewpoint, because  
5 it eliminates the otherwise necessary step of removing the catalyst residue from the polymer after completion of the polymerization. However, it is to be noted that the catalyst activity should be evaluated on the weight basis of transition metal as well as solid  
10 catalyst. Most of the catalysts comprising a transition metal compound such as titanium tetrachloride supported on a carrier such as a magnesium compound, which have recently been actively developed, are unsatisfactory with respect to the polymerization activity per unit  
15 quantity of the solid catalyst. On the other hand, the polymer build-up on the wall of polymerization vessel should be as little as possible, because it causes various operation troubles which lead to a decrease in operation efficiency. In the case of slurry polymerization  
20 or gas-phase polymerization, it is desirable in view of the steadiness and efficiency of the operation that the polymer powder has a high bulk density, narrow particle size distribution, and good flowability (a property of the particles to flow). In view of the above requirements,  
25 in the production of olefin polymers, a polymerization catalyst of industrial superiority is such that it has a sufficiently high activity on the weight basis of transition metal and solid catalyst to

1 omit the step of removing the catalyst residue, it causes  
little build-up of polymer on the wall of polymerization  
vessel, and it gives in slurry or gas-phase polymeriza-  
tion a polymer powder having a high bulk density and a  
5 high flowability. On the other hand, the molecular  
weight distribution of the resulting polymer is an  
important factor which controls the processability of  
the polymer as well as the appearance and physical  
properties of the fabricated articles. For instance,  
10 a polymer of narrow molecular weight distribution is  
suitable for injection molding or rotational molding,  
while that of broad molecular weight distribution is  
desirable for blow molding, extrusion molding, or  
film extrusion. Therefore, if it is possible to regulate  
15 easily the molecular weight distribution of a polymer  
by simple means, a great industrial advantage will be  
gained, because it then becomes possible to produce a  
wide variety of polymers suitable for particular uses.

It has been well known that a catalyst system  
20 (so-called Ziegler catalyst) comprising a combination  
of a compound of transition metals of Groups IVa to  
VIa of the periodic table and an organometallic compound  
of metals of Groups I to III is effective as the catalyst  
for olefin polymerization. These catalysts, however,  
25 do not always meet the above requirements and so  
cannot be called catalysts of industrial superiority,  
because of their low activity in general and, as a  
consequence, the necessity of removing the catalyst

- 1 residue from the polymerizate after completion of the polymerization.

Concerning the Ziegler catalyst, various improvements have heretofore been published. For instance, catalytic systems comprising combinations of an organoaluminum compound and a reduction product of a transition metal compound in normal maximum valence state with an organomagnesium compound have been disclosed [Japanese Patent Application "Kokai" (Laid-  
10 open) Nos. 4,392/71, 4,393/71 and 11,695/72]. Other disclosed methods and catalyst systems include a polymerization method in which at least a major portion of a tetravalent titanium compound is reduced with the reaction mixture of an organoaluminum halide and  
15 an organomagnesium compound and the resulting reduction product is activated with an organoaluminum compound before and/or after feeding to the polymerization zone (Japanese Patent Publication No. 11,672/76); a gas-phase polymerization method employing a catalyst prepared by  
20 reducing a transition metal compound in maximum valence state with a reducing mixture of an aluminum halide compound and an organomagnesium compound and mixing the resulting product with an organoaluminum compound as activator (Japanese Patent Publication No. 39,468/75);  
25 a catalyst system comprising an organometallic compound and a catalyst component prepared by treating a solid reaction product of a transition metal compound and an organomagnesium compound with a Lewis acid [Japanese

- 1 Patent Application "Kokai" (Laid-open) No. 126,785/75];  
a polymerization method, in which there is used a  
catalyst comprising the reaction product of (1) a tetra-  
or tri-valent titanium ester, (2) an organomagnesium  
5 compound, and (3) an organometal halide of a metal of  
Group IIIa of the periodic table [Japanese Patent  
Application "Kokai" (Laid-open) No. 143,883/75];  
a catalyst system comprising an organoaluminum  
compound and a product of the reaction between a  
10 Grignard reagent and a reaction mixture of a silicon  
halide and a transition metal halide (Japanese Patent  
Publication No. 1,321/81); a catalyst system comprising  
an organometallic compound and a reaction product  
obtained by heating (1) a hydroxylated organic compound,  
15 (2) metallic magnesium, (3) an oxygen-containing organic  
compound of a metal of Groups IVa, Va and VIa of the  
periodic table, (4) a halogen-containing compound of a  
metal of Groups IVa, Va and VIa of the periodic  
table, and (5) an aluminum halide compound (Japanese  
20 Patent Publication No. 39,714/77); a catalyst system  
comprising an organoaluminum compound and a solid  
reaction product of (1) a dihalide of magnesium,  
calcium, manganese, or zinc, (2) an oxygen-containing  
organic compound of titanium, zirconium or vanadium,  
25 and (3) an organoaluminum halide (Japanese Patent  
Publication No. 37,195/76); a catalyst system comprising  
an organoaluminum compound and a solid catalyst compound  
obtained by the reaction of a mixture in a specified

1 ratio of (1) an oxygen- or halogen-containing organic  
 compound of magnesium, (2) an oxygen- or halogen-  
 containing organic compound of titanium, (3) an oxygen-  
 or halogen-containing organic compound of zirconium,  
 5 and (4) an organoaluminum halide (Japanese Patent  
 Publication No. 8,083/80); a catalyst system comprising  
 an organometallic compound and a solid catalyst component  
 obtained by reacting a halogen- or alkoxy-containing  
 organoaluminum compound with a solid product derived  
 10 from the reaction of a halogen-containing compound of  
 titanium or vanadium with a reaction product of a hydro-  
 polysiloxane, a silicon compound containing an organic  
 group and hydroxyl group bonded to the silicon atom, and  
 a Grignard reagent (Japanese Patent Publication  
 15 No. 7,443/80); and a catalyst system comprising an  
 organometallic compound and a solid product obtained  
 by the reaction of (1) at least one member selected from  
 metallic magnesium and hydroxylated organic compounds,  
 oxygen-containing organic compounds of magnesium,  
 20 and halogen-containing magnesium compounds, (2) an  
 oxygen-containing organic compound of titanium or a  
 halogen-containing titanium compound, (3) an oxygen-  
 containing organic compound of zirconium or a halogen-  
 containing zirconium compound, (4) a silicon compound,  
 25 and (5) an aluminum halide compound [Japanese Patent  
 Application "Kokai" (Laid-open) No. 151,704/81]. These  
 improved catalyst systems, however, are yet unsatisfactory  
 from the industrial viewpoint with respect to polymerization

1 activity and powder characteristics of the polymer.

Moreover, a polymer of broad molecular weight distribution is not obtainable by use of these catalyst systems, except for those disclosed by Japanese Patent Publication  
5 Nos. 39,714/77 and 8,083/80 and Japanese Patent Application "Kokai" (Laid-open) No. 151,704/81.

The present inventors conducted an extensive study to develop a highly active and industrially advantageous catalyst for olefin polymerization and,  
10 as a result, found that a solid catalyst component having a high activity and other advantageous properties is obtained by reacting a silicon compound with a compound of a transition metal of Groups IVa, Va and VIa of the periodic table, further reacting the resulting reaction  
15 mixture with an organomagnesium compound, and contacting the resulting product with a halogen-containing compound of a transition metal of Groups IVa, Va and VIa of the periodic table to form a hydrocarbon-insoluble product to be used as the solid catalyst component; or  
20 by reacting a silicon compound with a compound of a transition metal of Groups IVa, Va and VIa of the periodic table, further reacting the resulting reaction mixture with an organomagnesium compound, then reacting the resulting reaction product with an organoaluminum  
25 halide compound represented by the general formula  $R^4_l AlX_{3-l}$  (wherein  $R^4$  is an organic group having 1 to 20 carbon atoms, X is a halogen atom, and l is a number defined by the formula  $0 < l < 3$ ), and contacting

- 1 the resulting reaction product with a halogen-containing compound of a transition metal f Groups IVa, Va and VIa of the periodic table to form a hydrocarbon-insoluble product to be used as the solid catalyst component.
- 5 The solid catalyst component thus obtained is highly active, is effective in reducing the polymer build-up on the wall of polymerization vessel, and permits of easy control of molecular weight distribution of the polymer. When the slurry or gas-phase polymerization
- 10 is carried out in the presence of this solid catalyst component, there is obtained a polymer powder of narrow particle size distribution comprising approximately spherical or elongated spherical particles having a high bulk density and good flowability. The present
- 15 invention has been accomplished based on the above finding.

An object of this invention is to provide a novel solid catalyst component for olefin polymerization.

Other objects and advantages of this invention

20 will become apparent from the following description.

According to this invention, there is provided

1. a solid catalyst component for olefin polymerization comprising a hydrocarbon-insoluble product (III) obtained by reacting

25 (A) a silicon compound selected from the group consisting of

(1) silicon compounds represented by the general formula  $R^1_a R^2_b R^3_c Si$ , wherein  $R^1$ ,  $R^2$  and  $R^3$

- 1 are each an alkyl, cycloalkyl, aralkyl, aryl,  
alkoxy, aryl xy, or hydroxyl group or a halogen  
or hydrogen atom; and a, b and c are numbers  
defined by the formulas  $0 \leq a \leq 4$ ,  $0 \leq b \leq 4$ ,  
5  $0 \leq c \leq 4$ , respectively, and  $a + b + c = 4$ ; and  
(2) silicon compounds containing the linkage  
Si-O-Si and polymers thereof

with

- (B) a compound of a transition metal of Groups IVa,  
10 Va and VIa of the periodic table to form a reaction  
mixture (I), further reacting the reaction mixture  
(I) with  
(C) an organomagnesium compound selected from simple  
organomagnesium compounds and hydrocarbon-soluble  
15 complexes thereof with an organometallic compound  
capable of solubilizing said organomagnesium  
compounds

to produce an intermediate product (II), and contacting  
the intermediate product (II) with

- 20 (D) a halogen-containing compound of a transition metal  
of Groups IVa, Va and VIa of the periodic table,  
to form the hydrocarbon-insoluble product (III); or

2. a solid catalyst component for olefin polymerization  
obtained by reacting said intermediate product (II) with

- 25 (E) an organoaluminum halide represented by the general  
formula  $R^4_l AlX_{3-l}$ , wherein  $R^4$  is an organic group  
having 1 to 20 carbon atoms, X is a halogen atom,  
and l is a number defined by the formula  $0 < l < 3$ ,

1 and contacting the resulting reaction product (IV) with  
(D) a halogen-containing compound of a transition  
metal of Groups IVa, Va and VIa of the periodic  
table.

5 The silicon compounds used as the component

(A)(1) according to this invention are those represented  
by the general formula  $R^1_a R^2_b R^3_c Si$ , wherein  $R^1$ ,  $R^2$  and  
 $R^3$  are each an alkyl, cycloalkyl, aralkyl, aryl, alkoxy,  
aryloxy, or hydroxy group or a halogen or hydrogen  
10 atom and a, b and c are numbers defined by the formulas  
 $0 \leq a \leq 4$ ,  $0 \leq b \leq 4$ ,  $0 \leq c \leq 4$ , respectively, and  $a + b + c = 4$ . As  
examples, mention may be made of  $Si(OCH_3)_4$ ,  $Si(OC_2H_5)_4$ ,  $Si(OC_3H_7)_4$ ,  
 $Si(OC_4H_9)_4$ ,  $Si(OC_6H_5)_4$ ,  $SiCl_4$ ,  $SiBr_4$ ,  $Si(OC_2H_5)_3Cl$ ,  
 $Si(OC_2H_5)_2Cl_2$ ,  $Si(OC_2H_5)Cl_3$ ,  $HSiCl_3$ ,  $CH_3SiCl_2H$ ,  $C_2H_5SiCl_3$ ,  
15  $C_6H_5SiCl_3$ ,  $(CH_3)_2SiCl_2$ ,  $(C_2H_5)_3SiOH$ ,  $(C_2H_5)_2Si(OH)_2$ ,  
 $(C_6H_5)_2Si(OH)_2$ , and  $C_4H_9Si(OH)_3$ . Preferable silicon  
compounds are those of the general formula, wherein  
 $R^1$  is an alkoxy or aryloxy group,  $R^2$  is a halogen  
atom,  $0 \leq a \leq 4$ ,  $0 \leq b \leq 4$ ,  $a + b = 4$  and  $c = 0$ . Most preferred  
20 are tetraalkoxysilanes such as  $Si(OC_2H_5)_4$  and silicon  
tetrahalides such as  $SiCl_4$ .

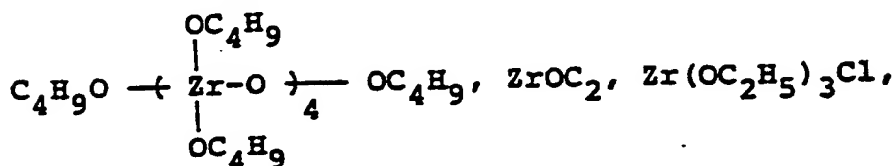
The silicon compounds used as the component

(A)(2) are those having at least one Si-O-Si linkage  
or polymers thereof. Examples include  $Si_2OCl_6$ ,  
25 hexamethyldisiloxane, tetramethyldisiloxane, tri-  
methylcyclotrisiloxane, dimethylpolysiloxane, diphenyl-  
polysiloxane, methylhydropolysiloxane, phenylhydro-  
polysiloxane, chlorophenylpolysiloxane, ethoxyhydropoly-

1 siloxane, and polysilanol. The polymers may have any of the chain, cyclic, and reticulate structures and any of the polymerization degrees.

The compounds of transition metals ( $M^1$ ) of Groups IVa, Va and VIa of the periodic table, used as the components (B), are those represented by the general formula  $[M^1O_p(OR^5)_qX_r]_m$ , wherein  $R^5$  is an organic group having 1 to 20 carbon atoms, X is a halogen atom, p is a number defined by the formula  $0 \leq p \leq 1.5$ , q and r are numbers defined by the formulas  $0 \leq q \leq 4$  and  $0 \leq r \leq 4$ , respectively, and m is an integer. Preferable compounds are those of the general formula in which  $0 \leq p \leq 1$  and  $1 \leq m \leq 10$ .  $R^5$  may be either saturated or unsaturated and may contain such atoms as halogen, silicon, oxygen, nitrogen, sulfur or phosphorus.  $R^5$  is selected preferably from alkyl, cycloalkyl, aryl, aralkyl, alkenyl, and acyl groups and substitution derivatives thereof.  $M^1$  is selected preferably from titanium, vanadium, zirconium, and hafnium, most preferably from titanium and zirconium. Examples of the compounds (B) include  $Ti(OC_2H_5)_4$ ,  $Ti(O-n-C_3H_7)_4$ ,  $Ti(O-iso-C_3H_7)_4$ ,  $Ti(O-n-C_4H_9)_4$ ,  $Ti(O-sec-C_4H_9)_4$ ,  $Ti(O-tert-C_4H_9)_4$ ,  $Ti(OC_6H_5)_4$ ,  $Ti(OC_6H_4CH_3)_4$ ,  $Ti(OC_6H_4Cl)_4$ ,  $TiO(OC_2H_5)_2$ ,  $C_4H_9O \begin{array}{c} OC_4H_9 \\ | \\ -Ti-O- \\ | \\ OC_4H_9 \end{array} \begin{array}{c} 4 \\ 4 \end{array} OC_4H_9$ ,  $TiOCl_2$ ,  $Ti(OC_2H_5)_3Cl$ ,  $Ti(OC_2H_5)_2Cl_2$ ,  $Ti(OC_2H_5)Cl_3$ ,  $Ti(OC_6H_5)Cl_3$ ,  $TiCl_4$ ,  $TiBr_4$ ,  $Zr(OC_2H_5)_4$ ,  $Zr(O-n-C_3H_7)_4$ ,  $Zr(O-iso-C_3H_7)_4$ ,  $Zr(O-n-C_4H_9)_4$ ,

- 1  $\text{Zr}(\text{O-sec-C}_4\text{H}_9)_4$ ,  $\text{Zr}(\text{O-tert-C}_4\text{H}_9)_4$ ,  $\text{Zr}(\text{OC}_6\text{H}_5)_4$ ,  
 $\text{Zr}(\text{OC}_6\text{H}_4\text{CH}_3)_4$ ,  $\text{Zr}(\text{OC}_6\text{H}_4\text{Cl})_4$ ,  $\text{ZrO}(\text{OC}_2\text{H}_5)_2$ ,



- $\text{Zr}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$ ,  $\text{Zr}(\text{OC}_2\text{H}_5)\text{Cl}_3$ ,  $\text{ZrCl}_4$ ,  $\text{ZrBr}_4$ ,  $\text{VOCl}_3$ ,  
 5  $\text{VCl}_4$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_3$ ,  $\text{VO}(\text{O-iso-C}_3\text{H}_7)_3$ ,  $\text{VO}(\text{O-n-C}_4\text{H}_9)_3$ ,  
 $\text{VO}(\text{O-iso-C}_4\text{H}_9)_3$ , and  $\text{HfCl}_4$ . Of these compounds,  
 especially preferred are those of the above formula in  
 which  $r = 0$ . It is also possible to use a combination  
 of two or more compounds (B). By use of a combination  
 10 of two or more compounds of different transition metals  
 ( $\text{M}^1$ ), it is possible to obtain a solid catalyst component  
 which gives a polymer of broad molecular weight  
 distribution. A combination suitable for this purpose  
 is that of Ti and Zr compounds. The suitable atomic  
 15 ratio, Ti:Zr, is generally from 1:50 to 50:1, preferably  
 from 1:20 to 20:1, most preferably from 1:10 to 10:1.

The organomagnesium compound (C) may be any  
 of the organomagnesium compounds having a magnesium-  
 carbon bond. Especially preferred are Grignard compounds  
 20 represented by the general formula  $\text{R}^6\text{MgX}$ , wherein  $\text{R}^6$   
 represents a hydrocarbon radical of 1 to 20 carbon atoms  
 and X represents a halogen atom and dialkylmagnesium  
 compounds or diarylmagnesium compounds represented by  
 the general formula  $\text{R}^7\text{R}^8\text{Mg}$ , wherein  $\text{R}^7$  and  $\text{R}^8$ , which  
 25 may be the same or different, represent each a hydro-  
 carbon radical having 1 to 20 carbon atoms. The organic

- 1 groups  $R^7$  and  $R^8$  include those alkyl, aryl, aralkyl and alkenyl groups which hav 1 to 20 carbon atoms such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-amyl, isoamyl, n-hexyl, n-octyl,  
5 2-ethylhexyl, phenyl, and benzyl. Examples of individual Grignard compounds include methylmagnesium chloride, ethylmagnesium chloride, ethylmagnesium bromide, ethylmagnesium iodide, n-propylmagnesium chloride, n-propylmagnesium bromide, n-butylmagnesium chloride,  
10 n-butylmagnesium bromide, sec-butylmagnesium chloride, sec-butylmagnesium bromide, tert-butylmagnesium chloride, tert-butylmagnesium bromide, n-amylmagnesium chloride, isoamylmagnesium chloride, phenylmagnesium chloride, and phenylmagnesium bromide. Examples of the compounds  
15 of the formula  $R^7R^8Mg$  are diethylmagnesium, di-n-propylmagnesium, diisopropylmagnesium, di-n-butylmagnesium, di-sec-butylmagnesium, di-tert-butylmagnesium, n-butyl-sec-butylmagnesium, di-n-amylmagnesium, and diphenylmagnesium. Alkyl- or aryl-magnesium-  
20 alkoxides or -aryloxides may also be used as organomagnesium compound.

The solvents generally used in the synthesis of the above organomagnesium compounds are those of the ether type such as, for example, diethyl ether, di-n-  
25 propyl ether, diisopropyl ether, di-n-butyl ether, diisobutyl ether, di-n-amyl ether, diisoamyl ether, di-n-hexyl ether, di-n-octyl ether, diphenyl ether, dibenzyl ether, phenetole, anisole, tetrahydrofuran,

1 and tetrahydropyran. It is also possible to use hydro-  
carbon solvents such as, for example, hexane, heptane,  
octane, cyclohexane, methylcyclohexane, benzene,  
toluene, and xylene, or mixtures of these hydrocarbons  
5 and ethers. The organomagnesium compound is used  
preferably in the form of ether solution or ether  
complex. It is advantageous to the production of polymer  
particles in the form of approximated sphere or elongated  
sphere having a narrow particle size distribution to  
10 use an ether having 6 or more carbon atoms or a cyclic  
ether. It is preferred to use a Grignard compound of  
the formula  $R^6MgCl$  in the form of an ether solution or  
ether complex. It is also possible to use as the com-  
ponent (C) a hydrocarbon-soluble complex of an organo-  
15 magnesium compound with an organometallic compound  
capable of solubilizing the organomagnesium compound.  
Examples of such organometallic compounds are those  
of lithium, beryllium, boron, aluminum or zinc.

The compounds of transition metals ( $M^2$ ) of  
20 Groups IVa, Va and VIa of the periodic table, used as  
the component (D) may be those represented by the general  
formula  $[M^2O_s(OR^9)_tX_u]_n$ , wherein  $R^9$  is an organic group  
having 1 to 20 carbon atoms, X is a halogen atom, s is  
a number defined by the formula  $0 \leq s \leq 1.5$ , t is a  
25 number defined by the formula  $0 \leq t \leq 3$ , u is a number  
defined by the formula  $1 \leq u \leq 4$ , and n is an integer.  
It is preferable to use those compounds of the general  
formula in which  $0 \leq s \leq 1$  and  $1 \leq n \leq 10$ .  $R^9$  may be

1 either saturated or unsaturated and may contain such  
 an element as halogen, silicon, oxygen, nitrogen,  
 sulfur or phosphorus.  $R^9$  is selected preferably from  
 alkyl, cycloalkyl, aryl, aralkyl, alkenyl, and acyl  
 5 groups and substitution derivatives thereof.  $M^2$  is  
 selected preferably from titanium, vanadium, zirconium  
 and hafnium, most preferably from titanium and zirconium.  
 Examples of the compounds used as the component (D)  
 include those halogen-containing compounds which are  
 10 listed above among the examples of compounds used as the  
 component (B). Especially preferred are titanium  
 halides, particularly titanium tetrachloride. It is  
 also possible to use a combination of two or more  
 compounds as the component (D). A polymer of broad  
 15 molecular weight distribution is obtained by using a  
 component (D) containing a transition metal ( $M^2$ )  
 different from that ( $M^1$ ) contained in the component (B).

The organoaluminum halides used as the compo-  
 nent (E) are those represented by the general formula  
 20  $R^4_l AlX_{3-l}$ , wherein  $R^4$  represents an organic radical,  
 particularly a hydrocarbon radical, having 1 to 20,  
 preferably 1 to 6, carbon atoms, X represents a halogen  
 atom, and  $l$  is a number defined by the formula  $0 < l < 3$ .  
 X is preferably a chlorine atom, and  $l$  is preferably  
 25 a number defined by  $1 \leq l \leq 2$ , most preferably  $l = 1$ .  
 $R^4$  is selected preferably from alkyl, cycloalkyl,  
 aryl, aralkyl, and alkenyl groups. As examples of  
 component (E), mention may be made of ethylaluminum

1 dichlorid , isobutylaluminum dichlorid , thylaluminum  
sesquichloride, isobutylaluminum sesquichlorid ,  
diethylaluminum monochloride, and isobutylaluminum  
monochloride. Of these compounds, particularly  
5 preferred are alkylaluminum dichlorides such as  
ethylaluminum dichloride and isobutylaluminum dichlorid .  
A mixture of two or more different organoaluminum  
halides as component (E) may also be used. It is also  
possible to adjust the halogen content by use of a  
10 trialkylaluminum such as triethylaluminum or triisobutyl-  
aluminum or a trialkenylaluminum in combination with  
an organoaluminum halide.

The synthesis of a solid catalyst component is  
carried out always under an inert gas atmosphere such  
15 as nitrogen or argon. The reaction between a silicon  
compound [component (A)] and a compound of a transition  
metal of Groups IVa, Va and VIa of the periodic table  
[component (B)] is allowed to proceed either without  
using a reaction medium or in a suitable solvent or  
20 diluent at a temperature of generally  $-50^{\circ}$  to  $150^{\circ}\text{C}$   
for several minutes to several hours. The order of  
the addition of both reactants is free of restriction,  
namely, (A) may be added to (B) or (B) may be added to  
(A) or both may be added simultaneously to the reaction  
25 medium. The ratio of (A) in terms of silicon atom  
to (B) in terms of transition metal ( $M^1$ ) atom is from  
1:50 to 50:1, preferably from 1:20 to 20:1, most  
preferably from 1:10 to 10:1. Examples of the solvents

1 suitable as the reaction media include aliphatic hydro-  
carbons such as pentane, hexane, heptane, and octane,  
aromatic hydrocarbons and its derivatives such as  
benzene, toluene, xylene, and chlorobenzene, alicyclic  
5 hydrocarbons such as cyclohexane and cyclopentane, and  
ethers such as diethyl ether, dibutyl ether, and tetra-  
hydrofuran. These solvents are used each alone or in  
combinations. The reaction mixture (I) is generally a  
homogeneous solution, but occasionally contains insoluble  
10 matters.

The reaction mixture (I) is then allowed to  
react with an organomagnesium compound (C) to obtain an  
intermediate product (II). This reaction proceeds  
by mixing the reaction mixture (I) and the reactant  
15 (C) as such or in a suitable solvent or diluent and  
keeping the resulting mixture at generally -70° to  
150°C, preferably -30° to 50°C for several minutes to  
several hours, preferably for 30 minutes to 5 hours.  
The order of the addition of both reactants is free  
20 of restriction, namely, (I) may be added to (C) or  
(C) may be added to (I) or both may be added simultane-  
ously to the reaction medium. The ratio of (I) in terms of  
the sum of silicon atom and transition metal atom to  
(C) in terms of magnesium atom is from 1:10 to 10:1,  
25 preferably from 1:5 to 5:1, most preferably from 1:2 to  
2:1. Examples of the solvents suitable as the reaction  
media include aliphatic hydrocarbons such as pentane,  
hexane, heptane and octane, aromatic hydrocarbons

1 such as benzen , toluen and xylene, alicyclic hydr -  
carbons such as cyclohexan and cyclop ntane, and thers  
such as ethyl ether, dibutyl ether, tetrahydrofuran,  
and dioxane. These solvents are used each alone or in  
5 combinations.

The intermediate product (II) thus obtained is,  
in most cases, a solid substance insoluble in the solvent,  
but is sometimes obtained as dissolved in the reaction  
medium, depending on the type of reactants and the  
10 solvent. The product in the solution form can be isolated  
as a solid by precipitating from the solution with a  
precipitant, by the temperature change, removal of the  
solvent by distillation, or reprecipitation.

The intermediate product (II) is then contacted  
15 with the component (D) either without being isolated  
or after having been isolated by evaporation of the  
reaction mixture to dryness or by filtration followed  
by drying or by filtration and subsequent thorough  
washing with a solvent. Alternatively, the intermeidate  
20 product (II) is allowed to react with the component (E),  
and then the resulting product is contacted with the  
component (D). The contact is effected either directly  
in the absence of a solvent or in a solvent or diluent  
at a temperature of generally -70° to 200°C, preferably  
25 -30° to 150°C, most preferably 30° to 140°C for several  
minut s to several hours. The order of the addition of  
both reactants is free of any restriction, namely, (D)  
may be added to (II), or (II) may be added to (D)

1 or both may be added simultaneously to the reaction  
medium. The ratio between (II) and (D) can be selected  
from a wide range.

If the amount of component (D) relative to  
5 intermediate product (II) is too small, the effect of  
the contact with component (D) is hardly exhibited,  
whereas if the component (D) is used in excess of  
the necessary amount, no additional advantage is gained.  
By changing the ratio between the intermediate product  
10 (II) and the component (D), it is possible to adjust the  
molecular weight distribution of the polymer. It is  
generally desirable to select the amount of (D) from  
the range of 0.01 to 10 mols for 1 g of the intermediate  
product (II). The solvents used in the reaction include  
15 aliphatic hydrocarbons such as, for example, pentane,  
hexane, heptane and octane; halohydrocarbons such as  
carbon tetrachloride and dichloroethane; aromatic  
hydrocarbons and its derivatives such as benzene, toluene,  
xylene, and chlorobenzene, and alicyclic hydrocarbons  
20 such as cyclohexane and cyclopentane. These solvents  
are used each alone or in mixtures.

The reaction between the intermediate product  
(II) and the component (E) is carried out by mixing  
both reactants as such or dissolved in or diluted with  
25 a suitable solvent and treating the mixture at a  
temperature of generally from -70° to 200°C, preferably  
from -30° to 150°C, most preferably from 30° to 100°C,  
for several minutes to several hours. The order of

1 addition of the reactants is not critical. The component  
(E) may be added to the intermediat product (II), or  
vice versa, or both reactants may be added simul-  
taneously to a reaction medium. The ratio between the  
5 intermediate product (II) and the component (E) may be  
selected from a wide range. By varying the ratio, it  
is possible to adjust the molecular weight distribution  
of the polymer. In general, with the increase in the  
ratio of component (E) to intermediate product (II),  
the molecular weight distribution of the polymer becomes broader.  
It is generally preferred to select the amount of component (E)  
in terms of the halogen atom from the range of 0.01 to 0.1 gram  
equivalent for 1 gram of the intermediate product (II). The examples  
of solvents used in the reaction include aliphatic  
15 hydrocarbons such as pentane, hexane, heptane, and  
octane; halohydrocarbons such as carbon tetrachloride  
and dichloroethane; aromatic hydrocarbons and its  
derivatives such as benzene, toluene, xylene and chloro-  
benzene; and alicyclic hydrocarbons such as cyclo-  
20 hexane and cyclopentane. These solvents are used each  
alone or in mixtures.

Before contacting with the component (D),  
the reaction product (IV) formed from the intermediate  
product (II) and the component (E) is usually collected  
25 by filtration and used as such or after drying, or after  
thorough washing with a solvent followed by drying or  
without drying. The contact between the reaction  
product (IV) and the component (D) is effected by

1 intermixing both materials as such or dissolved in or  
diluted with a suitable solvent, and keeping the mixture  
at a temperature of generally  $-70^{\circ}$  to  $200^{\circ}\text{C}$ , preferably  
 $-30^{\circ}$  to  $150^{\circ}\text{C}$ , most preferably  $30^{\circ}$  to  $140^{\circ}\text{C}$ , for several  
5 minutes to several hours. The order of the addition  
of both materials is not critical. The component (D)  
may be added to the reaction product (IV), or vice  
versa, or both may be mixed together all at a time.  
The ratio between both materials may be selected from a  
10 wide range. However, if the amount used of the  
component (D) relative to the amount of the reaction  
product (IV) is too small, the effect of the contact  
is hardly exhibited, whereas if it is in excess of the  
necessary amount, no additional advantage will be  
15 gained. By varying the ratio, it is possible to adjust  
the molecular weight distribution of the polymer. In  
general, a suitable amount of the component (D) for 1 g  
of the reaction product (IV) is 0.01 mmole to 1 mol,  
preferably 0.1 mmol to 0.1 mol, most preferably 1 mmol  
20 to 0.1 mol. Examples of the solvents used in the  
reaction include aliphatic hydrocarbons such as pentane,  
hexane, heptane, and octane, halohydrocarbons such as  
carbon tetrachloride and dichloroethane, aromatic hydro-  
carbons and its derivatives such as benzene, toluene,  
25 xylene, and chlorobenzene, and alicyclic hydrocarbons  
such as cyclohexane and cyclopentane. These solvents  
are used alone or in mixtures.

The hydrocarbon-insoluble product (III) thus

- 1 prepared is a powder comprising approximately spherical  
or longated spherical particles f narrow particle  
size distribution and good flowability. It contains  
magnesium, a transition metal of Grops IVa, Va and VIa  
5 of the periodic table, and a halogen atom. It is  
generally amorphous or feebly crystalline, showing,  
in most cases, scarcely any X-ray diffraction peak or  
only very broad or feeble diffraction peaks at  
interplanar spacings ( $d$ ) of around 5.9, 2.8 and 1.8 Å.  
10 The hydrocarbon-insoluble product (III) is usually  
collected by filtration, washed thoroughly with a hydro-  
carbon diluent, and used, either as such or after drying,  
as solid catalyst component for olefin polymerization.

- In polymerizing or copolymerizing an olefin,  
15 the hydrocarbon-insoluble reaction product (III) accord-  
ing to this invention is used in combination with an  
organometallic compound of a metal of Groups I, II and  
III of the perodic table. As examples of such organo-  
metallic compounds, mention may be made of organoaluminum  
20 compounds including trialkylaluminus such as triethyl-  
aluminum, tri-n-propylaluminum, tri-n-butylaluminum,  
triisobutylaluminum, and tri-n-hexylaluminum; dialkyl-  
aluminum monohalides such as diethylaluminum monochloride,  
di-n-propylaluminum monochloride, di-n-butylaluminum  
25 monochloride, diisobutylaluminum monochloride, and di-  
n-hexylaluminum monochloride; alkylaluminum dihalides  
such as ethylaluminum dichlorid , n-propylaluminum  
dichloride, n-butylaluminum dichloride, isobutylaluminum

1 dichloride, and n-hexylaluminum dichloride; alkylaluminum  
sesquihalides such as ethylaluminum sesquichloride,  
n-propylaluminum sesquichloride, n-butylaluminum  
sesquichloride, isobutylaluminum sesquichloride, and  
5 n-hexylaluminum sesquichloride; trialkenyl aluminums  
such as triisoprenylaluminum; alkoxyaluminums such as  
diethylaluminum ethoxide, dibutylaluminum butoxide, ethyl-  
aluminum sesquiethoxide, and butylaluminum sesquibutoxide;  
alkoxyaluminum halides such as ethylaluminum ethoxy-  
10 chloride and butylaluminum butoxychloride; alkylaluminum  
hydrides such as diethylaluminum hydride, dibutylaluminum  
hydride, ethylaluminum dihydride, and butylaluminum  
dihydride; organozinc compounds such as diethylzinc;  
organomagnesium compound such as diethylmagnesium and  
15 ethylmagnesium chloride; and  $\text{LiAl}(\text{C}_2\text{H}_5)_4$ . Of these  
compounds, especially preferred are trialkylaluminums,  
alkylaluminum halides, or mixtures thereof.

The solid catalyst component of this invention  
is suitable for use in the polymerization of terminally  
20 unsaturated olefins having 2 to 20, preferably 2 to 10,  
carbon atoms such as, for example, ethylene, propylene,  
butene-1, 4-methylpentene-1, hexene-1 and octene-1. It  
is also suitable for the copolymerization of two or  
more of these olefins and the copolymerization of  
25 these olefins with diolefins having 4 to 20 carbon atoms  
such as, for example, 1,4-hexadiene, 1,7-octadiene,  
vinylcyclohexene, 1,3-divinylcyclohexene, cyclopentadiene,  
1,5-cyclooctadiene, dicyclopentadiene, norbornadiene,

1 5-vinylnorbornene, thylidenenorbornen, butadiene, and  
isoprene. The present solid catalyst component is  
advantageously adaptable especially to the homopoly-  
merization of ethylene or copolymerization of 90 mole-%  
5 or more of ethylene with other olefins such as pre-  
ferably propylene, butene-1, 4-methylpentene-1, hexene-1,  
and octene-1. For the purpose of adjusting the stereo-  
regularity and molecular weight distribution, an electron-  
donating compound such as those containing nitrogen,  
10 oxygen, or phosphorus can be added to the polymerization  
system.

The polymerization can be carried out by the  
customary method of slurry polymerization, gas-phase  
polymerization, solution polymerization, or melt  
15 polymerization. When the method of slurry polymeriza-  
tion, or gas-phase polymerization is used, there is  
obtained a polymer powder in the particle form of approxi-  
mated sphere or elongated sphere, corresponding to the  
desirable particle form of the present solid catalyst com-  
20 ponent, and the polymer powder has a narrow particle  
size distribution, a high bulk density, and a good  
flowability.

The polymerization temperature is generally  
from room temperature to 200°C, preferably 40° to 150°C  
25 and the polymerization pressure is from atmospheric to  
100 atmospheres, preferably atmospheric to 50 atmospheres,  
though the polymerization proceeds normally at higher  
temperatures and pressures. It is possible to use a

1 molecular weight regulator such as, for example, hydrogen.  
The polymerization is carried out either continuously  
or batchwise. It is also feasible to carry out multi-  
stage polymerization using a solid catalyst component of  
5 this invention by means of a combination of multiple  
reaction zones of different polymerization conditions.  
A sufficient concentration of the present solid catalyst  
component in the polymerization system is usually 0.001  
to 1 millimoles of the transition metal atom per 1 liter  
10 of the reaction medium or of the polymerization vessel.  
The organometallic compound as catalyst component is used  
in an amount within range of 0.5 to 500, preferably 2 to  
100, mole equivalents per mole of transition metal atom  
in the solid catalyst component. The inert solvents  
15 used as polymerization solvent in slurry polymerization  
and solution polymerization include aliphatic  
hydrocarbons such as propane, butane, pentane, hexane,  
heptane, and octane and alicyclic hydrocarbons such  
as cyclohexane and cycloheptane. It is also possible  
20 to use as the polymerization solvent the polymerizable  
monomers such as ethylene, propylene, butene-1,  
4-methylpentene-1, hexene-1, and octene-1 themselves.

When the present solid catalyst component  
is used in the olefin polymerization, owing to a  
25 high activity of the catalyst per unit quantity of the  
transition metal as well as per unit quantity of the  
solid catalyst, the residual catalyst content of the  
resulting polymer becomes so small that the step of its

1 removal is unnecessary; moreover the polymer build-up  
on the wall of polymerization vessel is much reduced.  
When slurry polymerization or gas-phase polymerization  
is carried out, there is formed a polymer powder  
5 comprising approximately spherical or elongated sphere-  
like particles having a narrow particle size distribution  
and a desirable flowability, which no longer requires  
pelletization. Thus, the polymerization efficiency  
is high and the operation steps are simplified. Since  
10 the molecular weight of the resulting polymer can  
be controlled by properly selecting the type and quantity  
of each component used in the preparation of the present  
solid catalyst component, it is possible to prepare  
various polymers suitable for a wide range of specific  
15 uses such as injection molding, rotational molding,  
extrusion molding, film extrusion, and blow molding.

The invention is further illustrated below in  
detail with reference to Examples, but the invention is  
not limited thereto, unless it departs from the  
20 essential feature of the invention. In Examples, the  
polymer properties were tested as described below.

The density and bulk density were tested  
according to the methods specified in JIS K 6760  
and K 6721, respectively.

25 The melt flow ratio (MFR) was used as a  
measure for the melt flowability. According to the  
method for testing melt index specified in ASTM D 1238-  
57T, MFR is expressed as a ratio of the flow rate under

1 a load of 2.160 kg to that (MI) under a load f 21.60 kg:

$$\text{MFR} = \frac{\text{Flow rate under 21.60 kg load}}{\text{Flow rate under 2.160 kg load}} .$$

It has been known that, in general, the broader the molecular weight distribution, the larger the value of MFR.

## 5 Example 1

### (1) Synthesis of organomagnesium compound.

Into a 1-liter flask provided with a stirrer, reflux condenser, dropping funnel, and thermometer, was placed 32.0 g of magnesium turnings for Grignard reagent. After removing the air and moisture from the flask by the thorough flushing with nitrogen, 120 g of n-butyl chloride and 500 ml of di-n-butyl ether were charged into the dropping funnel. About 30 ml of the mixture in the dropping funnel was added dropwise onto the magnesium to initiate the reaction. The dropwise addition of the remainder of the mixture was continued at 50°C for about 4 hours. After completion of the addition, the mixture in the flask was allowed to react for another hour at 60°C. The reaction mixture was then cooled down to room temperature and the insolubles were removed by filtration. The concentration of n-butyilmagnesium chloride in the di-n-butyl ether (filtrate) was found to be 2.03 moles/liter, as determined by the hydrolysis of n-butyilmagnesium chloride

1 with 1N sulfuric acid followed by the back-titration  
with 1N aqueous sodium hydroxide solution using  
phenolphthalin as the indicator.

(2) Syntheses of reaction mixture (I) and inter-  
5 mediate product (II).

To a solution of 3.00 g (8.78 mmol) of  
 $\text{Ti}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4$  in 30 ml of n-heptane, was added 5.49 ml  
[8.78 mmol of  $\text{Zr}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4$ ] of a solution of  $\text{Zr}(\text{O}-\text{n}-\text{C}_4\text{H}_9)_4$   
in n-heptane. To the mixture, after having been stirred  
10 for 15 minutes at room temperature, was added dropwise  
at room temperature 9.15 g (43.9 mmol) of  $\text{Si}(\text{OC}_2\text{H}_5)_4$   
over a period of 15 minutes. The mixture was then  
stirred at room temperature for 20 minutes to yield  
the reaction mixture (I) as a pale yellow homogeneous  
15 solution. To the reaction mixture (I), while being  
cooled at 5°C, was added dropwise over a period of  
35 minutes 30.3 ml (61.5 mmol) of a solution of  
 $\text{n}-\text{C}_4\text{H}_9\text{MgCl}$  in n-butyl ether prepared above in (1).  
With the dropwise addition, the reaction mixture turned  
20 brown and a solid product precipitated out. After  
completion of the dropwise addition, the reaction was  
allowed to continue for further two hours. After removing  
the liquid phase, by filtration the solid product was  
washed 5 times with 120 ml of n-heptane, and dried at room  
25 temperature under reduced pressure to yield 10.6 g of  
the intermediate product (II) as a brown powder. Ele-  
mentary analysis: 3.2% Ti, 6.1% Zr, 12.4% Mg, 17.1% Cl,  
and 0.7% of  $(\text{n}-\text{C}_4\text{H}_9)_2\text{O}$  (all percentages ar by weight).

*P. J. O.*  
*P. J. O.*

1 (3) Synthesis of solid catalyst component.

To 5.0 g of the intermediate product (II) prepared above in (2), was added at room temperature dropwise over a period of 30 minutes 15 ml of  $\text{TiCl}_4$ . *11.38*

5 After completion of the dropwise addition, the reaction was allowed to continue for another hour at 100°C. After completion of the reaction and removal of the liquid phase by filtration, the solid product was washed 5 times with 80 ml of n-heptane, and dried at  
10 room temperature under reduced pressure to yield 4.7 g of the reaction product (III) as a brown powder. Upon analysis, the reaction product (III) was found to contain 6.5% Ti, 5.4% Zr, 12.2% Mg, and 65.0% Cl. The X-ray diffraction pattern of this powder showed  
15 only weak broad diffraction peaks in the vicinity of interplanar spacings (d) of 5.9, 2.8 and 1.8 Å. The microscopic observation revealed that the powder particles were approximately spherical and showed a narrow particle size distribution.

20 (4) Polymerization of ethylene.

Into a 1-liter autoclave provided with an electromagnetic induction stirrer, which had been thoroughly flushed with nitrogen, were added 500 ml of n-heptane and 1.0 mmol of triisobutylaluminum.

25 Into the autoclave, after the temperature had been elevated to 80°C, was charged hydrogen to a total pressure of 3 kg/cm<sup>2</sup> followed by ethylene to a total pressure of 13 kg/cm<sup>2</sup>. The polymerization was initiated

1 by the addition of 3.3 mg of the solid catalyst component  
prepared above in (3). Ethylene was continuously fed  
to the autoclave to maintain the total pressure constant  
at 80°C for one hour. After the addition of 2 ml of  
5 isobutyl alcohol to terminate the polymerization, the  
polymer which was formed was collected by filtration  
and dried at 60°C under reduced pressure. The yield of  
polymer amounted to 60.4 g. The polymerization activity  
was 18,300 g polymer/g solid catalyst/hour and 154,000 g  
10 polymer/g transition metal/hour. The polymer had a  
melt index of 0.59 g/10 minutes, MFR of 56, and bulk  
density of 0.41 g/cm<sup>3</sup>. The polymer powder was  
approximately spherical in particle shape and showed  
a narrow particle size distribution and good flowability.

15 Example 2

The polymerization of ethylene was carried out  
in the same manner as in Example 1 (4), except that  
1.0 mmol of triethylaluminum was used in place  
of the triisobutylaluminum and 3.5 mg of the solid  
20 catalyst component was used. There were obtained 56.7 g  
of the polymer. The catalyst activity was 16,200 g  
polymer/g solid catalyst/hour and 136,000 g polymer/g  
transition metal/hour. The MI of the polymer was  
1.2 g/10 minutes, MFR 51, and the bulk density 0.40 g/cm<sup>3</sup>.  
25 The particles of the polymer powder were approximately  
spherical and showed a narrow particle size distribution  
and good flowability.

1 Example 3

The polymerization of ethylene was carried out in the same manner as in Example 1 (4), except that there were used 1.0 mmol of diethylaluminum monochloride in place of the triisobutylaluminum, 11.5 mg of the solid catalyst component, a hydrogen pressure of 10 kg/cm<sup>2</sup>, and a total pressure of 20 kg/cm<sup>2</sup>. There were obtained 53.4 g of the polymer. The catalyst activity was 4,630 g polymer/g solid catalyst/hour and 38,900 g polymer/g transition metal/hour. The polymer had a MI of 0.31 g/10 minutes, MFR of 60 and a bulk density of 0.42 g/cm<sup>3</sup>. The polymer powder was approximately spherical in particle shape and showed a markedly narrow particle size distribution and good flowability.

15 Example 4

Into a 1-liter autoclave provided with an electromagnetic induction stirrer, which had been thoroughly flushed with nitrogen, were charged 50 ml of n-heptane, 1.0 mmol of triisobutylaluminum and 10 g of butene-1. Into the autoclave, after the temperature had been elevated to 80°C, was charged hydrogen to a total pressure of 2 kg/cm<sup>2</sup> followed by ethylene to a total pressure of 12 kg/cm<sup>2</sup>. The polymerization was initiated by the addition of 2.7 mg of the solid catalyst component prepared in Example 1 (3). Ethylene was charged continuously to the autoclave to maintain the total pressure constant at 80°C for 1 hour to effect

1 the copolymerization of ethylen with butene-1. After  
completion of the polymerization, the copolymer which  
was formed was collected by filtration and dried at  
60°C under reduced pressure. The yield of copolymer  
5 was 58.9 g. The catalyst activity was 21,800 g polymer/g  
solid catalyst/hour and 183,000 g polymer/g transition  
metal/hour. The copolymer contained 4.2 ethyl groups  
per 1,000 carbon atoms. It showed a density of 0.941  
g/cm<sup>3</sup>, MI of 0.48 g/10 minutes, MFR of 53 and a bulk  
10 density of 0.42 g /cm<sup>3</sup>. The polymer powder was  
approximately spherical in particle shape and showed a  
narrow particle size distribution and good flowability.

#### Comparative Example 1

The polymerization of ethylene was carried  
15 out in the same manner as in Example 1 (4), except that  
17.8 mg of the intermediate product (II) prepared in  
Example 1 (2) was used as the solid catalyst component.  
There was obtained only a trace amount of a polymer.

#### Comparative Example 2

20 The polymerization of ethylene was carried out  
in th same manner as in Example 3, except that 13.1 mg  
of the intermediate product (II) prepared in Example 1  
(2) was used as the solid catalyst component. There  
was obtained 28.0 g of a polymer. The catalyst activity  
25 was 2,140 g polymer/g solid catalyst/hour and  
23,000 g polymer/g transition metal/hour. The polymer

1 had MI of 0.67 g/10 minutes, MFR of 34, and a bulk density  
of 0.24 g/cm<sup>3</sup>. As compared with the results obtained in  
Example 3, the catalyst activity was inferior and the  
polymer powder was inferior in bulk density and flowabi-  
5 lity and showed a narrower molecular weight distribution.

### Comparative Example 3

#### (1) Synthesis of solid catalyst component.

To a solution of 21.8 g (105 mmol) of  $\text{Si}(\text{OC}_2\text{H}_5)_4$   
in 30 ml of n-heptane, while being maintained at 5°C, was  
10 added dropwise over a period of 35 minutes 51.6 ml  
(105 mmol  $\text{n-C}_4\text{H}_9\text{MgCl}$ ) of a di-n-butyl ether solution  
containing  $\text{n-C}_4\text{H}_9\text{MgCl}$  prepared in Example 1 (1). The  
mixture was then allowed to continue the reaction at  
room temperature for 2 more hours. The liquid phase was  
15 then removed by filtration and the solid phase was  
washed 5 times with 120 ml of n-heptane and dried at  
room temperature under reduced pressure to yield 13.3 g  
of a white powder. To a 6.1 g portion of the white  
powder, was added dropwise 18 ml of  $\text{TiCl}_4$  at room tem-  
20 perature over a period of 30 minutes. The mixture was  
then brought to 100°C and allowed to react for one  
hour. After completion of the reaction, the liquid  
phase was removed by filtration and the solid phase  
was washed 5 times with 120 ml of n-heptane and dried at  
25 room temperature under reduced pressure to yield  
5.8 g of a pale yellow powder which, upon analysis, was  
found to contain 6.0% by weight of titanium.

1 (2) Polymerization of ethylene.

The polymerization of ethylene was carried out in the same manner as in Example 1 (4), except that 3.9 mg of the pale yellow powder obtained above in 5 (1) was used as the solid catalyst component. There were obtained 52.3 g of a polymer. The catalyst activity was 12,400 g polymer/g solid catalyst/hour and 207,000 g polymer/g transition metal/hour. The polymer had MI of 0.62 g/10 minutes, MFR of 37 and a bulk 10 density of 0.29 g/cm<sup>3</sup>. The molecular weight distribution was narrow and the polymer powder was unsatisfactory in bulk density and flowability.

Comparative Example 4

(1) Synthesis of solid catalyst component.

15 To a solution of 10.0 g (29.3 mmol) of Ti(O-n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> in 30 ml of n-heptane, was added 18.3 ml [29.3 mmol Zr(O-n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>] of a solution of Zr(O-n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> in n-heptane. The mixture was stirred for 10 minutes at room temperature. To the mixture, while being 20 maintained at 5°C, was added dropwise over a period of 35 minutes 28.8 ml (58.6 mmol n-C<sub>4</sub>H<sub>9</sub>MgCl) of a solution of n-C<sub>4</sub>H<sub>9</sub>MgCl prepared in Example 1 (1) in n-butyl ether. With the dropwise addition, the reaction mixture turned brown and a solid product was formed. 25 After completion of the addition, the mixture was allowed to continue the reaction at room temperature for two more hours. The liquid phase was then removed

1 by filtration, and the solid product was washed 5 times  
with 200 ml of n-heptane and dried at room temperature  
under reduced pressure to yield 13.2 g of a brown  
powder. A 5.7 g portion of the powder was weighed out  
5 and 17 ml of  $\text{TiCl}_4$  was added thereto dropwise at room  
temperature over a period of 30 minutes. After the  
addition was completed, the mixture was brought to  $100^\circ\text{C}$   
and was allowed to react for one hour. After completion  
of the reaction, the liquid phase was removed by filtra-  
10 tion and the solid product was washed 5 times with 60 ml  
of n-heptane and dried at room temperature under reduced  
pressure to yield 4.3 g of a brown powder which was  
found, upon analysis, to contain 11.2% by weight of  
titanium and 16.9% by weight of zirconium.

15 (2) Polymerization of ethylene.

The polymerization of ethylene was carried out  
in the same manner as in Example 1 (4), except that 4.3 mg  
of the brown powder was used as the solid catalyst  
component. There were obtained 61.5 g of a polymer.  
20 The catalyst activity was 14,300 g polymer/g solid  
catalyst/hour and 59,900 g polymer/g transition  
metal/hour. The polymerization activity per g  
transsition metal was unsatisfactory. The polymer  
was found to have MI of 0.38 g/10 minutes, MFR of  
25 44, and a bulk density of  $0.26 \text{ g/cm}^3$ . The polymer  
was unsatisfactory with respect to the bulk density  
and flowability.

## 1   Comparativ   Example 5

## (1)   Synth sis of solid catalyst component.

A solid catalyst component was prepared by use of the same compounds in the same ratios as in Example 1 (2) and (3), but by a different procedure for synthesizing the intermediate product (II).

To a solution of 9.15 g (43.9 mmol) of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  in 30 ml of n-heptane, while being maintain d at 5°C, was added dropwise over a period of 35 minutes 10 30.3 ml (61.5 mmol n- $\text{C}_4\text{H}_9\text{MgCl}$ ) of the n-butyl ether solution of n- $\text{C}_4\text{H}_9\text{MgCl}$  prepared in Example 1 (1). With the dropwise addition, there was formed a white solid product. After the addition, the mixture was allowed to continue the reaction for another hour at 5°C. To the resulting 15 suspension, while being maintained at 5°C, was added dropwise over a period of 30 minutes 10 ml of a n-heptane solution containing 8.7 mmol of  $\text{Ti}(\text{O-n-C}_4\text{H}_9)_4$  and 8.7 mmol of  $\text{Zr}(\text{O-n-C}_4\text{H}_9)_4$  which had been prepared in advance. With the dropwise addition, the suspension was 20 turned brown. After completion of the addition, th mixture was allowed to continue the reaction for 2 more hours at room temperature. The liquid phase was removed by filtration and the solid product was washed 5 times with 120 ml of n-heptane and dried at room 25 temperature to yield 9.4 g of a brown powder which was found, upon analysis, to contain 3.5% by weight of titanium and 5.4% by weight of zirconium. A 5.3 g portion of the brown powder was weighed out and 16 ml

1 of titanium tetrachloride was added dropwise thereto at  
room temperature over a period of 30 minutes. After the  
addition, the mixture was brought to 100°C and was allowed  
to react for one hour. After completion of the reaction,  
5 the liquid phase was removed by filtration and the solid  
product was washed 5 times with 60 ml of n-heptan and  
dried at room temperature under reduced pressure to  
yield 4.1 g of a brown powder which was found, upon  
analysis, to contain 9.3% by weight of titanium and  
10 9.3% by weight of zirconium.

(2) Polymerization of ethylene.

The polymerization of ethylene was carried out  
in the same manner as in Example 1 (4), except that  
8.0 mg of brown powder synthesized above in (1) was  
15 used as the solid catalyst component. There were  
obtained 83.2 g of a polymer. The catalyst activity was  
10,400 g polymer/g solid catalyst/hour and 83,900 g  
polymer/g transition metal/hour. The polymer was found  
to have MI of 0.51 g/10 minutes, MFR of 38, and a bulk  
20 density of 0.23 g/cm<sup>3</sup>. The polymer had a narrow molecular  
weight distribution and the polymer powder showed a  
broad particle size distribution and was unsatisfactory  
in bulk density and powder flowability.

Examples 5 to 12

25 In a manner similar to that in Example 1,  
various solid catalyst components were prepared from  
various compounds and the polymerization of ethylene was

1 carried out in the presence of these solid catalyst  
components. The conditions for the preparation of  
these solid catalyst components were as shown in Table 1  
and the results of ethylene polymerization were as  
5 shown in Table 2.

Table 1

Example No.	Preparation of intermediate product (II)			
	Component (A)		Component (B)	
	Compound	Amount used (Si gram atom)	Compound	Amount used (mol)
5	Si(OEt) <sub>4</sub>	0.066	Ti(O-n-Bu) <sub>4</sub>	0.006
			Zr(O-n-Bu) <sub>4</sub>	0.060
6	SiCl <sub>4</sub>	0.095	Zr(O-n-Bu) <sub>4</sub>	0.019
7	Si(OEt) <sub>4</sub>	0.090	Ti(O-n-Bu) <sub>4</sub>	0.030
8	Si(O-i-Pr) <sub>4</sub>	0.085	Ti(O-n-Pr) <sub>4</sub>	0.014
			Zr(O-n-Pr) <sub>4</sub>	0.071
9	[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> O	0.06	Ti(OEt) <sub>4</sub>	0.006
			Zr(O-n-Pr) <sub>4</sub>	0.030
10	Dimethylpoly-siloxane (25°C, 100 cSt)	0.150	Ti(OEt) <sub>4</sub>	0.015
			VO(OEt) <sub>3</sub>	0.015
11	Methylhydrogenpolysiloxane (25°C, 30 cSt)	0.060	VO(OEt) <sub>3</sub>	0.030
12	Si(OEt) <sub>4</sub>	0.070	Ti(O-n-Bu) <sub>4</sub>	0.012
			Zr(O-n-Bu) <sub>4</sub>	0.058

- Cont'd -

Note: Et = C<sub>2</sub>H<sub>5</sub>, n-Pr = n-C<sub>3</sub>H<sub>7</sub>, i-Pr = iso-C<sub>3</sub>H<sub>7</sub>,  
n-Bu = C<sub>4</sub>H<sub>9</sub>, sec-Bu = sec-C<sub>4</sub>H<sub>9</sub>

Table 1 (Cont'd)

			Preparation of hydro-carbon insoluble product (III)	
Component (C)		Reaction medium	Component (D)	
Compound (reaction medium)	Amount used (mol)		Compound	Amount used (mmol/g product (II))
n-BuMgCl ((n-Bu) <sub>2</sub> O)	0.132	n-heptane	TiCl <sub>4</sub>	20
( " )	0.114	"	"	15
( " )	0.120	"	"	20
i-PrMgCl ((i-Pr) <sub>2</sub> O)	0.170	Toluene	Ti(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Cl	15
n-BuMgCl ((n-Bu) <sub>2</sub> O)	0.096	(n-Bu) <sub>2</sub> O	TiCl <sub>4</sub>	20
( " )	0.180	n-heptane	"	"
(tetrahydro-furan)	0.090	"	Ti(OC <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Cl	15
(n-Bu) Mg (sec-Bu) (n-heptane)	0.140	"	TiCl <sub>4</sub>	20

- Cont'd -

Table 1 (C nt'd)

Reaction medium	Transition metal content of product (III) (% by weight)	
-	Ti	10.2
	Zr	13.4
-	Ti	3.3
	Zr	9.3
Toluene	Ti	6.2
Chloro-benzene	Ti	3.2
	Zr	7.3
-	Ti	5.3
	Zr	10.2
-	Ti	5.7
	V	3.2
Chloro-benzene	Ti	3.1
	V	6.3
-	Ti	4.0
	Zr	14.1

Table 2

Exam- ple No.	Amount of solid catalyst component (mg)	Organo- metallic compound	Poly- meriza- tion temp. (°C)	Yield of poly- mer (g)	Catalyst activity		Bulk den- sity (g/ cm <sup>3</sup> )	MI (g/ 10 min.)	MFR
					g polymer/ g solid catalyst/ hour	g polymer/g transition metal/hour			
5	3.7	Triiso- butyl- aluminum	80	58.8	15,900	67,300	0.40	0.35	63
6	2.7	"	"	60.5	22,400	178,000	0.39	0.62	57
7	3.1	"	"	59.2	19,100	308,000	0.40	0.65	33
8	4.1	"	"	61.9	15,100	144,000	0.39	0.27	54
9	3.4	"	"	56.7	16,700	108,000	0.41	0.39	48
10	3.3	"	"	64.0	19,400	218,000	0.39	0.59	46
11	3.5	"	"	57.1	16,300	173,000	0.36	0.61	40
12	3.9	"	"	53.8	13,800	76,200	0.33	0.40	51

1 Comparative Example 6

(1) Synthesis of solid catalyst component.

In the synthesis of solid catalyst component, the same compounds and the same material ratios as in Example 12 were used, but the procedure for the synthesis of intermediate product (II) was different.

To a solution of 5.0 g (67.4 mmol in terms of silicon atom) of dimethylpolysiloxane (100 centistokes in viscosity at 25°C) in 30 ml of n-heptane, while being maintained at 5°C, was added dropwise over a period of 35 minutes 39.9 ml (80.9 mmol n-C<sub>4</sub>H<sub>9</sub>MgCl) of the di-n-buthyl ether solution of n-C<sub>4</sub>H<sub>9</sub>MgCl prepared in Example 1 (1). With the dropwise addition, there was formed a white solid product. After the addition, the mixture was allowed to continue the reaction at 5°C for another hour. To the resulting suspension, while being maintained at 5°C, was added dropwise over a period of 30 minutes 10 ml of a n-heptane solution containing each 6.74 mmol of Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and VO(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. With the dropwise addition, the suspension of reaction mixture turned brown. After the addition, the mixture was allowed to continue the reaction at room temperature for 2 more hours. The liquid phase was then removed by filtration and the solid phase was washed 5 times with 120 ml of n-heptane and dried at room temperature under reduced pressure to yield 9.1 g of a brown powder which, upon analysis, was found to contain 2.8% by weight of titanium and 3.5% by weight of vanadium. To a 6.1 g of portion of the powder, was

1 added at room temperature dropwise 16.8 ml of  $\text{TiCl}_4$  over  
a period of 30 minutes. The mixture was then brought to  
100°C and allowed to react for another hour. After  
completion of the reaction, the liquid phase was removed  
5 by filtration and the solid phase was washed 5 times with  
60 ml of n-heptane and dried at room temperature under  
reduced pressure to yield 4.0 g of a brown powder which,  
upon analysis, was found to contain 7.2% by weight of  
titanium and 3.4% by weight of vanadium.

10 (2) Polymerization of ethylene.

The polymerization was carried out in the same  
manner as in Example 1 (4), except that 7.1 mg of the  
brown powder prepared above in (1) was used as the solid  
catalyst component. There were formed 68.9 g of a poly-  
15 mer. The catalyst activity was 9,700 g polymer/g solid  
catalyst/hour and 91,500 g polymer/g transition metal/  
hour. The polymer showed MI of 0.57 g/10 minutes, MFR  
of 37, a bulk density of 0.24, and a narrow molecular  
weight distribution. The polymer powder showed a broad  
20 particle size distribution and was very unsatisfactory  
in bulk density and powder flowability.

Example 13

(1) Synthesis of organomagnesium compound.

A di-n-butyl ether solution of  $n\text{-C}_4\text{H}_9\text{MgCl}$   
25 (2.03 mol/liter) was prepared in a similar manner to  
Example 1 (1).

(2) Synthesis of reaction mixture (I) and intermediate

1 product (II).

To a solution of 7.47 g (21.9 mmol) of  $\text{Ti}(\text{O}-\text{n-C}_4\text{H}_9)$  in 150 ml of n-heptane, was added 58.7 ml [109 mmol  $\text{Zr}(\text{O}-\text{n-C}_4\text{H}_9)_4$ ] of a solution of  $\text{Zr}(\text{O}-\text{n-C}_4\text{H}_9)_4$  in  
5 n-heptane. The mixture was stirred at room temperature for 10 minutes. To the mixture, was added dropwise 27.3 g (131 mmol) of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  over a period of 15 minutes at room temperature. The mixture was stirred at room temperature for 20 minutes to form a pale yellow homogeneous  
10 ous solution [reaction mixture (I)]. To the reaction mixture (I), while being maintained at 5°C, was added dropwise over a period of two hours 129 ml (262 mmol n- $\text{C}_4\text{H}_9\text{MgCl}$ ) of the di-n-buthyl ether solution of n- $\text{C}_4\text{H}_9\text{-MgCl}$  prepared above in (1). With the dropwise addition,  
15 the reaction mixture turned brown and a solid product was formed. After the addition, the mixture was allowed to continue the reaction at 5°C for another hour, then at room temperature for 2 more hours.. The liquid phase was then removed by filtration and the solid phase was  
20 washed 5 times with 250 ml of n-heptane and dried at room temperature under reduced pressure to yield 60.6 g of a brown powder [intermediate product (II)] which, upon analysis, was found to contain 2.1% of titanium, 17.2% of zirconium, 11.6% of magnesium, 16.1% of chlorine,  
25 and 0.7% of di-n-buthyl ether (all percentages are by weight).

(3) Synthesis of solid catalyst component.

To a mixture of 50 g of the intermediate product

1 (II) prepared above in (2) and 145 ml of n-heptane , was  
added at 60°C dropwise over a period of 3 hours 289 ml  
(1 mol  $C_2H_5AlCl_2$ ) of a solution of  $C_2H_5AlCl_2$  in n-heptane.  
The mixture was then allowed to react at 65°C for one  
5 hour. After completion of the reaction, the liquid phase  
was removed by filtration and the solid phase was washed  
5 times with 250 ml of n-heptane and dried at room  
temperature under reduced pressure to yield 35 g of a  
brownish black powder [product (IV)] which, upon analysis,  
10 was found to contain 2.3% of titanium, 18.0% of zircon-  
ium, 8.9% of magnesium, 54.0% of chlorine, and 3.4% of  
aluminum (all percentages are by weight). To a 3.0 g  
portion of the product (IV), was added at room temperature  
15 15 ml (137 mmol) of  $TiCl_4$ . The mixture was brought to  
100°C and allowed to react for one hour. After complection  
of the reaction, the liquid phase was removed by filtra-  
tion and the solid phase was washed 5 times with 80 ml  
of n-heptane and dried at room temperature under reduced  
pressure to yield 4.0 g of a brown powder [product(III)]  
20 which, upon analysis, was found to contain 11.4% of tita-  
nium, 10.3% of zirconium, 6.2% of magnesium, 60.3% of  
chlorine, and 1.8% of aluminum (all percentages are by  
weight). The powder gave an X-ray diffraction diagram  
in which only weak and broad diffraction peaks were ob-  
25 servable at interplanar spacings (d) of about 5.9, 2.8  
and 1.8 Å. The powder particles were found by microscop-  
ic examination to be approximately spherical in shape  
and of narrow particle size distribution.

1 (4) Polymerization of ethylene.

Into a 1-liter autoclave provided with an electromagnetic induction stirrer, which had been thoroughly flushed with nitrogen, were charged 500 ml of n-  
5 heptane and 1.0 mmol of triisobutylaluminum. After the internal temperature had been elevated to 80°C, hydrogen was charged to a total pressure of 5 kg/cm<sup>2</sup> followed by ethylene to a total pressure of 15 kg/cm<sup>2</sup>. The polymerization was initiated by adding 3.6 mg of the solid  
10 catalyst component [product (III)] prepared above in (3). The polymerization was allowed to continue at 80°C for one hour, while feeding ethylene continuously to keep the total pressure constant. After completion of the polymerization, the polymer was collected by filtration  
15 and dried at 60°C under reduced pressure to yield 65.8 g of a polymer. The polymerization activity was 18,300 g polymer/g solid catalyst/hour and 84,200 g polymer/g transition metal/hour. The polymer showed MI of 0.41 g/10 minutes, MFR of 84, and bulk density of 0.39 g/cm<sup>3</sup>.  
20 The polymer particles were approximately spherical and of a narrow particle size distribution indicative of good flowability.

Example 14

The polymerization of ethylene was carried out  
25 in the same manner as in Example 13, except that 1.0 mmol of triethylaluminum was used in place of the triisobutylaluminum and the amount of the solid catalyst component

1 was 4.1 mg. There were obtained 63.6 g of a polymer.  
The catalyst activity was 15,500 g polym r/g solid catal-  
yst/hour and 71,500 g polymer/g transition metal/hour.  
The polymer showed MI of 0.33 g/10 minutes, MFR of 78,  
5 and a bulk density of 0.38 g/cm<sup>3</sup>. The polymer particles  
were approximately spherical in shape and of a narrow  
particle size distribution indicative of a good flowabil-  
ity.

#### Example 15

10 The polymerization of ethylene was carried out  
in the same manner as in Example 13 (4), except that  
1.0 mmol of diethylaluminum monochloride was used in place  
of the triisobutylaluminum, the amount used of the solid  
catalyst component was 10.0 mg, and the hydrogen pressure  
15 and total pressure were 10 kg/cm<sup>2</sup> and 20 kg/cm<sup>2</sup>, respec-  
tively. There were obtained 57.9 g of a polymer. The  
catalyst activity was 5,790 g polymer/g solid catalyst/  
hour and 26,700 g polymer/g transition metal/hour.  
The polymer showed MI of 0.25 g/10 minutes, MFR of 67,  
20 and a buk density of 0.41 g/cm<sup>3</sup>. The polymer particl s  
were approximately spherical and of a very narrow  
particle size distribution indicative of a good  
flowability.

#### Example 16

25 Into a 1-liter autoclave provided with an elec-  
tromagnetic induction stirrer, which had been thorou-

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1 ghly flushed with nitrogen, were charged 200 g of butane,  
1.0 mmol of triisobutylaluminum, and 50 g of butene-1.  
After the internal temperature had been elevated to 70°C,  
hydrogen was charged to a total pressure of 5 kg/cm<sup>2</sup> and  
5 ethylene was then fed to a total pressure of 15 kg/cm<sup>2</sup>.  
Polymerization was initiated by the addition of 3.4 mg  
of the solid catalyst component [product (III)] prepared  
in Example 13 (3). The copolymerization of ethylene and  
butene-1 was allowed to proceed at 70°C for one hour,  
10 while maintaining the total pressure constant by the  
continuous feeding of ethylene. After completion of the  
polymerization, the polymer formed was collected by  
filtration and dried at 60°C under reduced pressure.  
The yield of polymer was 60.7 g. The catalyst activity  
15 was 17,900 g polymer/g solid catalyst/hour and 82,300 g  
polymer/g transition metal/hour. The copolymer contained  
18.4 ethyl groups per 1,000 carbon atoms and showed a  
density of 0.925 g/cm<sup>3</sup>, MI of 0.39 g/10 minutes, MFR of  
85, and a bulk density of 0.37 g/cm<sup>3</sup>. The polymer parti-  
20 cles were approximately spherical and of a narrow parti-  
cle size distribution indicating good flowability.

#### Comparative Example 7

The polymerization of ethylene was carried out  
in the same manner as in Example 13 (4), except that 17.0  
25 mg of the intermediate product (II) prepared in Example  
13 (2) was used as the solid catalyst component. Only a  
trace amount of polymer was obtained.

## 1 Comparative Example 8

The polymerization of ethylene was carried out in the same manner as in Example 13 (4), except that 8.9 mg of the product (IV) prepared in Example 13 (2) was used as the solid catalyst component. There were obtained 54.3 g of a polymer. The catalyst activity was 6,100 g polymer/g solid catalyst/hour and 28,100 g polymer/g transition metal/hour. The polymer showed MI of 0.08 g/10 minutes, MFR of 92, and a bulk density of 0.39 g/cm<sup>3</sup>.

## 10 Examples 17 to 20

A series of hydrocarbon-insoluble products (III) were prepared using the reaction product (IV) prepared in Example 13 and varied amounts of titanium tetrachloride. n-Heptane was used as the reaction medium in an amount of 4.5 ml for 1 g of the reaction product (IV). Titanium tetrachloride was added to the product (IV) at room temperature and the mixture was treated at 80°C for one hour. The solid product which was formed was washed with n-heptane and dried at room temperature under reduced pressure. Using the resulting solid catalyst component, ethylene was polymerized as in Example 13 (4). The conditions for the preparation of solid catalyst component [product (III)] and the results of ethylene polymerization were as shown in Table 3.

## 25 Example 21 to 30

In a manner similar to that in Example 13,

- 1 solid catalyst components were prepared using various compounds. The conditions for the synthesis and the results of ethylene polymerization were as shown in Tables 4 and 5, respectively.

Table 3

Exam- ple No.	Preparation of product (III)			Polymerization of ethylene					
	Amount of TiCl <sub>4</sub> used [mmol/g product (IV)]	Transition metal con- tent of product (III) (% by weight)	Amount of solid catalyst compo- nent (mg)	Yield of poly- mer (g)	Catalyst activity		Bulk den- sity (g/ cm <sup>3</sup> )	MI (g/ 10 min.)	MFR
					g Polymer/ g solid catalyst/ hour	g Polymer/g transition metal/hour			
17	10	Ti 11.3 Zr 10.0	3.5	63.2	18,100	84,800	0.39	0.40	86
18	4	Ti 10.6 Zr 12.0	3.8	59.5	15,700	69,300	0.40	0.38	90
19	2	Ti 9.9 Zr 13.4	3.9	54.7	14,000	60,200	0.39	0.27	98
20	0.5	Ti 5.0 Zr 16.1	5.6	57.0	10,200	48,200	0.39	0.13	104

Table 4

Example No.	Preparation of product (II)			
	Component (A)		Component (B)	
	Compound	Amount used (Si gram atom)	Compound	Amount used (mol)
21	Si(OEt) <sub>4</sub>	0.131	Ti(O-n-Bu) <sub>4</sub> Zr(O-n-Bu) <sub>4</sub>	0.022 0.109
22	"	"	Ti(O-n-Bu) <sub>4</sub> Zr(O-n-Bu) <sub>4</sub>	0.022 0.109
23	Si(O-n-Bu) <sub>4</sub>	0.085	Ti(O-n-Bu) <sub>4</sub> Zr(O-n-Bu) <sub>4</sub>	0.028 0.057
24	"	0.080	Ti(O-n-Bu) <sub>4</sub>	0.016
25	"	"	Zr(O-n-Bu) <sub>4</sub>	"
26	SiCl <sub>4</sub>	"	Ti(O-n-Bu) <sub>4</sub> Zr(O-n-Pr) <sub>4</sub>	0.020 0.060
27	Dimethyl-polysiloxane (25°C, 100 cSt)	"	Ti(OEt) <sub>4</sub> Vo(OEt) <sub>3</sub>	0.040 0.040
28	[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> O	0.085	TiCl <sub>4</sub> Zr(O-n-Pr) <sub>4</sub>	0.028 0.057
29	SiCl <sub>4</sub>	0.090	TiCl <sub>4</sub>	0.030
30	"	0.100	"	0.050

Note: Et = C<sub>2</sub>H<sub>5</sub>, n-Pr = n-C<sub>3</sub>H<sub>7</sub>, i-Pr = iso-C<sub>3</sub>H<sub>7</sub>,  
 n-Bu = n-C<sub>4</sub>H<sub>9</sub>, sec-Bu = sec-C<sub>4</sub>H<sub>9</sub>,  
 i-Bu = iso-C<sub>4</sub>H<sub>9</sub>

- Cont'd -

Table (Cont'd)

			Preparation of product (IV)		
Component (C)		Reaction medium	Component (E)		Reaction medium
Compound (reaction medium)	Amount used (mol)		Compound	Amount used [mmol/g product (II)]	
n-BuMgCl ((n-Bu) <sub>2</sub> O)	0.262	n-heptane	EtAlCl <sub>2</sub>	15	n-heptane
" ( " )	"	"	"	25	"
" ( " )	0.170	"	"	20	"
" ( " )	0.096	"	"	"	"
" ( " )	"	"	"	"	"
(n-Bu)Mg (sec-Bu) (n-heptane)	0.180	"	i-BuAlCl <sub>2</sub>	15	"
n-BuMgCl (Tetrahydrofuran)	0.160	Toluene	Et <sub>2</sub> AlCl	30	Toluene
i-PrMgCl ((i-Pr) <sub>2</sub> O)	0.096	(n-Bu) <sub>2</sub> O	EtAlCl <sub>2</sub>	20	"
n-BuMgCl ((n-Bu) <sub>2</sub> O)	0.120	n-heptane	"	"	n-heptane
" ( " )	0.150	"	"	"	"

- Cont'd -

Table 4 (Cont'd)

Preparation of product (III)		Reaction medium	Transition metal content of product (III) (% by weight)	
Component (D)				
Compound	Amount used [mmol/g product (IV)]			
TiCl <sub>4</sub>	46	-	Ti	11.0
			Zr	10.0
"	"	-	Ti	11.5
			Zr	10.7
"	"	-	Ti	10.8
			Zr	9.8
"	"	-	Ti	10.4
"	"	-	Ti	8.7
			Zr	11.2
"	"	-	Ti	10.2
			Zr	10.7
Ti(OC <sub>6</sub> H <sub>5</sub> )Cl <sub>3</sub>	10	Chloro-benzene	Ti	12.3
			V	5.7
TiCl <sub>4</sub>	10	n-heptane	Ti	10.9
			Zr	10.1
Zr(O-n-Bu) <sub>2</sub> Cl <sub>2</sub>	20	-	Ti	8.4
			Zr	5.3
VOCl <sub>3</sub>	"	n-heptane	Ti	9.5
			V	4.0

Table 5

Exam- ple No.	Amount of solid catalyst component (mg)	Organo- metallic compound	Poly- meriza- tion temp (°C)	Yield of poly- mer (g)	Catalyst activity		Bulk den- city (g/ cm <sup>3</sup> )	MI (g/ 10 min.)	MFR
					g polymer/ g solid catalyst/ hour	g polymer/g transition metal/hour			
21	3.0	Triiso- butyl- aluminum	80	57.3	19,100	91,000	0.40	0.60	68
22	4.1	"	"	50.8	12,400	55,800	0.39	0.11	90
23	2.7	"	"	55.2	20,400	99,200	0.40	0.55	71
24	2.5	"	"	60.5	24,200	233,000	0.40	1.03	39
25	3.7	"	"	53.6	14,500	72,800	0.39	0.24	95
26	2.5	"	"	54.6	21,800	104,000	0.34	0.60	62
27	3.6	"	"	51.0	14,200	78,700	0.34	0.83	50
28	3.8	"	"	59.3	15,600	74,300	0.38	0.39	75
29	4.6	"	"	58.5	12,700	92,800	0.35	0.26	54
30	4.0	"	"	52.9	13,200	98,000	0.33	1.27	51

WHAT IS CLAIMED IS;

1. A solid catalyst component for olefin polymerization comprising a hydrocarbon-insoluble product (III) obtained by reacting

(A) a silicon compound selected from the group consisting of

- (1) silicon compounds represented by the general formula  $R^1_a R^2_b R^3_c Si$ , wherein  $R^1$ ,  $R^2$  and  $R^3$  are each an alkyl, cycloalkyl, aralkyl, aryl, alkoxy, aryloxy, or hydroxyl group or a halogen or hydrogen atom; and a, b and c are numbers defined by the formulas  $0 \leq a \leq 4$ ,  $0 \leq b \leq 4$ ,  $0 \leq c \leq 4$ , respectively, and  $a + b + c = 4$ ; and
- (2) silicon compounds containing the linkage Si-O-Si and polymers thereof

with

- (B) a compound of a transition metal of Groups IVa, Va and VIa of the periodic table to form a reaction mixture (I) further reacting the reaction mixture (I) with
- (C) an organomagnesium compound selected from simple organomagnesium compounds and hydrocarbon-soluble complexes thereof with an organometallic compound capable of solubilizing said organomagnesium compounds to produce an intermediate product (II), and contacting the intermediate product (II) with
- (D) a halogen-containing compound of a transition metal of Groups IVa, Va and VIa of the periodic table, to form the hydrocarbon-insoluble product (III).

2. A solid catalyst component for olefin polymerization according to Claim 1, wherein a reaction product (IV) produced by the reaction of the intermediate product (II) and (E) an organoaluminum halide represented by the general formula  $R^4_1AlX_{3-1}$  (wherein  $R^4$  is an organic group having 1 to 20 carbon atoms, X is a halogen atom, and 1 is a number defined by the formula  $0 < 1 < 3$ ) is contacted with (D) a halogen-containing compound of a transition metal of Groups IVa, Va and VIa of the periodic table.

3. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the component (A) is a silicon compound of the general formula  $R^1_a R^2_b R^3_c Si$  (wherein  $R^1$  is an alkoxy or aryloxy group,  $R^2$  is a halogen atom, and a, b and c are numbers defined by the formulas  $0 \leq a \leq 4$ ,  $0 \leq b \leq 4$ ,  $a + b = 4$  and  $c = 0$ ).

4. A solid catalyst component for olefin polymerization according to Claim 3, wherein the component (A) is a tetraalkoxysilane or tetraaryloxysilane.

5. A solid catalyst component for olefin polymerization according to Claim 3, wherein the component (A) is silicon tetrachloride.

6. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the component (A) is a polysiloxane.

7. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the component

(B) is a compound represented by the general formula  $[M^1 O_p (OR^5)_q X_r]_m$ , wherein  $M^1$  is a transition metal of Groups IVA, Va and VIA of the periodic table,  $R^5$  is an organic group having 1 to 20 carbon atoms, X is a halogen atom, p is a number defined by the formula  $0 \leq p \leq 1.5$ , q and r are numbers defined by the formulas  $0 \leq q \leq 4$  and  $0 \leq r \leq 4$  and m is an integer.

8. A solid catalyst component for olefin polymerization according to Claim 7, wherein  $M^1$  is an element selected from titanium, vanadium, zirconium and hafnium.

9. A solid catalyst component for olefin polymerization according to Claim 7, wherein  $M^1$  is selected from titanium and zirconium.

10. A solid catalyst component for olefin polymerization according to Claim 7, wherein a combination of two or more compounds containing different transition metals ( $M^1$ ) is used as the component (B).

11. A solid catalyst component for olefin polymerization according to Claim 10, wherein a combination of titanium and zirconium or of titanium and vanadium is used as the transition metal ( $M^1$ ).

12. A solid catalyst component for olefin polymerization according to Claim 11, wherein the atomic ratio of titanium to zirconium is from 1:50 to 50:1.

13. A solid catalyst component for olefin polymerization according to Claim 11, wherein the atomic

ratio of titanium to zirconium is from 1:20 to 20:1.

14. A solid catalyst component for olefin polymerization according to Claim 11, wherein the atomic ratio of titanium to zirconium is from 1:10 to 10:1.

15. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the component (C) is a compound represented by the general formula  $R^6MgX$ , wherein  $R^6$  is a hydrocarbon radical having 1 to 20 carbon atoms and X is a halogen atom, or  $R^7R^8Mg$ , wherein  $R^7$  and  $R^8$  are each a hydrocarbon radical having 1 to 20 carbon atoms.

16. A solid catalyst component for olefin polymerization according to Claim 15, wherein the component (C) is used in the form of ether solution or ether complex.

17. A solid catalyst component for olefin polymerization according to claim 16, wherein the ether is an ether having 6 or more carbon atoms or an ether having a cyclic structure.

18. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the component (D) is a compound represented by the general formula  $[M^2O_s(OR^9)_tX_u]_n$ , wherein  $M^2$  is a transition metal of Groups IVa, Va and VIa of the periodic table,  $R^9$  is an organic group having 1 to 20 carbon atoms, X is a halogen atom, s is a number defined by the formula  $0 \leq s \leq 1.5$ , t is a number defined by the formula  $0 \leq t \leq 3$ , u is a number defined by the formula  $1 \leq u \leq 4$ , and n is an integer.

19. A solid catalyst component for olefin polymerization according to Claim 18, wherein  $M^2$  is an element selected from titanium, vanadium, zirconium and hafnium.
20. A solid catalyst component for olefin polymerization according to Claim 18, wherein  $M^2$  is selected from titanium and zirconium.
21. A solid catalyst component for olefin polymerization according to Claim 18, wherein  $M^2$  is titanium.
22. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the component (D) is titanium tetrachloride.
23. A solid catalyst component for olefin polymerization according to Claim 2, wherein the component (E) is an alkylaluminum dichloride represented by the general formula  $R^4AlCl_2$ , wherein  $R^4$  is an alkyl group having 1 to 20 carbon atoms.
24. A solid catalyst component for olefin polymerization according to Claim 2, wherein the component (E) is ethylaluminum dichloride.
25. A solid catalyst component for olefin polymerization according to Claim 2, wherein the component (E) is isobutylaluminum dichloride.
26. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the intermediate product (II) is isolated from the reaction mixture.
27. A solid catalyst component for olefin

polymerization according to Claim 2, wherein the reaction product (IV) is isolated from the reaction mixture.

28. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the ratio of the component (A) in terms of silicon atom to the component (B) in terms of transition metal atom is in the range of from 1:50 to 50:1.

29. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the ratio of the component (A) in terms of silicon atom to the component (B) in terms of transition metal atom is in the range of from 1:20 to 20:1.

30. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the ratio of the reaction mixture (I) in terms of the sum of silicon atom and transition metal atom to the component (C) in terms of magnesium atom is in the range of from 1:2 to 2:1.

31. A solid catalyst component for olefin polymerization according to Claim 1 or 2, wherein the quantity of the component (D) for 1 g of the intermediate product (II) is in the range of from 0.01 to 10 mols.

32. A solid catalyst component for olefin polymerization according to Claim 2, wherein the quantity of the component (E) in terms of halogen atom for 1 g of the intermediate product (II) is in the range of from 0.01 to 0.1 gram equivalent.

33. A solid catalyst component for olefin polymerization according to Claim 2, wherein the quantity of the component (D) for 1 g of the reaction product (IV) is in the range of from 1 mmol to 0.1 mol.

34. A process for the preparation of a solid catalyst component for olefin polymerization, which comprises reacting

(A) a silicon compound selected from the group consisting of

(1) silicon compounds represented by the general formula  $R_a^1 R_b^2 R_c^3 Si$ , wherein  $R^1$ ,  $R^2$  and  $R^3$  are each an alkyl, cycloalkyl, aralkyl, aryl, alkoxy, aryloxy, or hydroxyl group or a halogen or hydrogen atom; and a, b and c are numbers defined by the formulas  $0 \leq a, b, c \leq 4$  and  $a + b + c = 4$ ; and

(2) silicon compounds containing the linkage Si-O-Si and polymers thereof

with

(B) a compound of a transition metal of Groups IVa, Va and VIa of the periodic table to form a reaction mixture (I), further reacting the reaction mixture (I) with

(C) an organomagnesium compound selected from simple organomagnesium compounds and hydrocarbon-soluble complexes thereof with an organometallic compound capable of solubilizing said organomagnesium compounds to produce an intermediate product (II),

and contacting the intermediate product (II) with  
(D) a halogen-containing compound of a transition metal  
of Groups IVa, Va and VIa of the periodic table,  
to form a hydrocarbon-insoluble product (III) to  
be used as the solid catalyst component.

35. A process for the preparation of a solid catalyst  
component for olefin polymerizaoin according to Claim  
34, wherein the intermediate product (II) is reacted  
with

(E) an organoaluminum halide represented by the general  
formula  $R^4_l AlX_{3-l}$ , wherein  $R^4$  is an organic group  
having 1 to 20 carbon atoms, X is a halogen atom,  
and l is a number defined by the formula  $0 < l < 3$ ,  
and the resulting reaction product (IV) is contacted  
with

(D) a halogen-containing compound of a transition metal  
of Groups IVa, Va and VIa of the periodic table.

36. A process for producing olefin polymers,  
which comprises polymerizing an olefin in the presence of  
the solid catalyst component according to Claim 1 and  
an organoaluminum compound.

37. A process for producing olefin polymers, which  
comprises polymerizing an olefin in the presence of the  
solid catalyst component according to Claim 2 and an  
organoaluminum compound.



European Patent  
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# EUROPEAN SEARCH REPORT

**0087100**  
Application number

EP 83 10 1402

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	CHEMICAL ABSTRACTS, vol. 91, no. 16, October 1979, page 18, no. 124230y, Columbus, Ohio, USA  & JP - A - 79 62192 (ASAHI CHEMICAL INDUSTRY CO., LTD.) 18-05-1979 * Abstract *	1,3,7- 9,15, 18-22, 34,36	C 08 F 10/00 C 08 F 4/62
X	--- GB-A-1 554 460 (SUMITOMO)  * Claims 1-26 *	1,2,5, 7-9,15 -25,34 -37	
X	--- GB-A-2 056 998 (ASAHI)  * Claims 1-5, 10-12, 22-27, 31; page 2, line 36 - page 3, line 50 *	1,3,7- 9,15, 18-22, 29,34, 36	TECHNICAL FIELDS SEARCHED (Int. Cl. 7)  C 08 F
E	--- EP-A-0 045 885 (MONTEDISON)  * Claims 1,4,7; page 5, lines 1-7; page 6, line 4 - page 7, line 4 *	1,3-11, 15-25, 34,36	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>02-06-1983</b>	Examiner <b>WEBER H.</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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